PURIFICATION OF HYDROCARBONS BY CRYSTALLIZATION FROM LIQUID METHANE. ISOLATION OF 2-METHYLHEPTANE FROM PETROLEUM [1]

By R. T. Leslie [2]

ABSTRACT

A method for purifying difficultly crystallizable hydrocarbons of low freezing points by crystallization from liquid methane has been developed. It consists in mixing the hydrocarbon with propane, ethane, ethylene, or other such low-boiling hydrocarbon and adding the mixture dropwise to liquefied methane. If a solid phase forms, it is separated from the liquid with the aid of a centrifuge and the volatile solvent recovered.

Apparatus for using the method on quantities up to approximately 100 ml has been devised.

A sample of 2-methylheptane was separated from petroleum, and its properties determined. It constitutes about 0.15 percent of the crude oil. The freezing point of 2-methylheptane is −111.3° C. Its infrared absorption spectrum was also obtained.

CONTENTS

I. INTRODUCTION

While crystallization is a valuable aid in the separation of hydrocarbons having boiling points which lie close together, many such hydrocarbon mixtures crystallize with difficulty or not at all. The absence of any strong tendency for the molecules to orient coupled with the high viscosity of the liquid suggest themselves as interfering factors. It should therefore be possible to encourage crystallization by the addition of substances which will produce a system of lower viscosity at low temperatures.

Such a problem was met in the separation of the constituents of petroleum from a fraction boiling between 115° and 120° C. This portion was found difficult to fractionate further by distillation, and cooling merely resulted in the formation of glasses below −100° C.

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project no. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

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Such a behavior is to be expected in view of the number of isomeric octanes and naphthenes with boiling points in this range. Few freezing points are reported for isomeric octanes which have been prepared synthetically, probably partly because of this difficulty of crystallization.

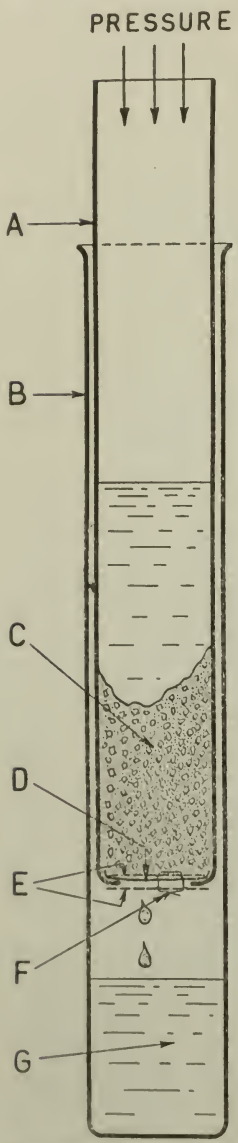

FIGURE 1.—*Apparatus for treating small quantities of material.*

A, filter tube; *B*, containing tube; *C*, solid phase; *D*, filter cloth or paper; *E*, perforated metal disks; *F*, wire holding plates together; *G*, liquid phase.

II. DEVELOPMENT OF THE METHOD

As diluents for these fractions, other hydrocarbons with low boiling points meet most satisfactorily the requirements of low viscosity at very low temperatures and easy subsequent separation. Dilution with propane at temperatures below its boiling point (−45° C.) was first tried, but was found to yield a mass on cooling below −120° C. which, though apparently somewhat crystalline in some cases, was too viscous for manipulation. Ethane and ethylene were tried with similar results. Consideration of methane showed that its boiling point (−161° C.) was below the congealing point of the fractions, and the addition of the petroleum fractions, which had been cooled as far as possible without congealing, to methane at temperatures below −161° C. resulted in a stiff glassy material which showed no signs of crystallization or solution. In order to get the fraction into solution in methane it was therefore mixed with sufficient ethane (below −88° C.) to give a mixture of moderately low viscosity at temperatures below the boiling point of methane. Addition of this mixture to methane resulted in the precipitation of a distinctly crystalline material, leaving a mobile liquid phase which was readily separable. While the mixture of petroleum fraction and ethane yielded the more satisfactory precipitate, it was found that ethylene or propane could also be used. For the work described in this paper, commercial propane and methane condensed from natural gas were used.

III. APPARATUS FOR TREATING SMALL QUANTITIES

For treatment of quantities less than 50 ml, the simple filter tube shown in figure 1 served to separate the phases. Methane was poured or condensed into *B* to the depth of 5 or 6 cm with the filter tube *A* resting on the bottom of *B*. A precooled mixture of the hydrocarbon with approximately an equal volume of propane was made by cooling the hydrocarbon in solid carbon dioxide and condensing or pouring in the propane. This mixture was further cooled below the boiling point of methane and added to the

methane dropwise while stirring. It was found best to transfer the cold liquids by forcing them by air pressure through vacuum-jacketed tubes in the manner in which liquid air is transferred. As soon as the methane reached saturation with respect to the least soluble constituent, the solution became turbid and continued to thicken as more hydrocarbon-propane mixture was added. The quantity which could be added depended on the hardness and filterability of the precipitate. If a glassy precipitate separated, it was found that the addition of more propane to the petroleum hydrocarbon sometimes improved the result. The liquid was filtered from the solid by raising the filter tube a few centimeters from the bottom of the containing tube, as shown in the figure, and applying a gentle air pressure. After the liquid was blown from the filter tube, the latter was transferred to a second containing tube similar to *B* which had been cooled to liquid-air temperature. Both tubes were then connected to a condensing train and the low-boiling hydrocarbons recovered by distillation. Most of the propane was caught in a solid-carbon-dioxide trap and the methane in a liquid-air trap.

Caution must be observed in all the manipulations which have been described in which hydrocarbons are brought into proximity to liquid air, especially in glass apparatus. Solid carbon dioxide supplemented by liquid nitrogen is advised whenever feasible. The presence of methane or propane in liquid air is readily detectable by the soapy appearance of the mixture. The high volatility of liquid methane and propane should be kept in mind and free flames or sparks should be avoided. Moving parts likely to become charged statically should be grounded. Care should also be taken not to allow liquid methane to come into contact with the skin since it causes freezing much more rapidly than liquid air, apparently because of a wetting effect.

The natural gas which was used as a source of methane was transported in light metal tanks having pressure gages attached. (Such tanks are obtainable on the market as "gas sample tanks.") Larger tanks, such as household hot-water reservoirs, were used for storage while the smaller tanks were in shipment. The condensation of the gases from the reservoirs was carried out under a pressure of 50 or 60 pounds.

For the treatment of larger quantities of material the apparatus shown in figure 2 was used. It was essentially a basket centrifuge designed to operate economically with regard to cooling agent at liquid-air temperatures and which was sufficiently gas-tight to permit recovery of the volatile gases contained in it. The gases were rectified for subsequent use in the condensing train shown in figure 3.

IV. CONSTRUCTION OF THE CENTRIFUGAL APPARATUS

The centrifuge shell *I* of figure 2 was constructed of brass tube of such dimensions that it could be completely contained in a Pyrex dewar tube with about a quarter of an inch clearance. The apparatus used in this work was 7 cm in diameter at the top of the shell and 34 cm in height. Quantities of petroleum hydrocarbon up to 100 ml could be treated in it. The cover was constructed of bakelite and arranged for ready locking in position with the minimum of interfering projection either inside or outside the shell. The lower bakelite disk *J* had three projections which were slipped under cleats *H* of the

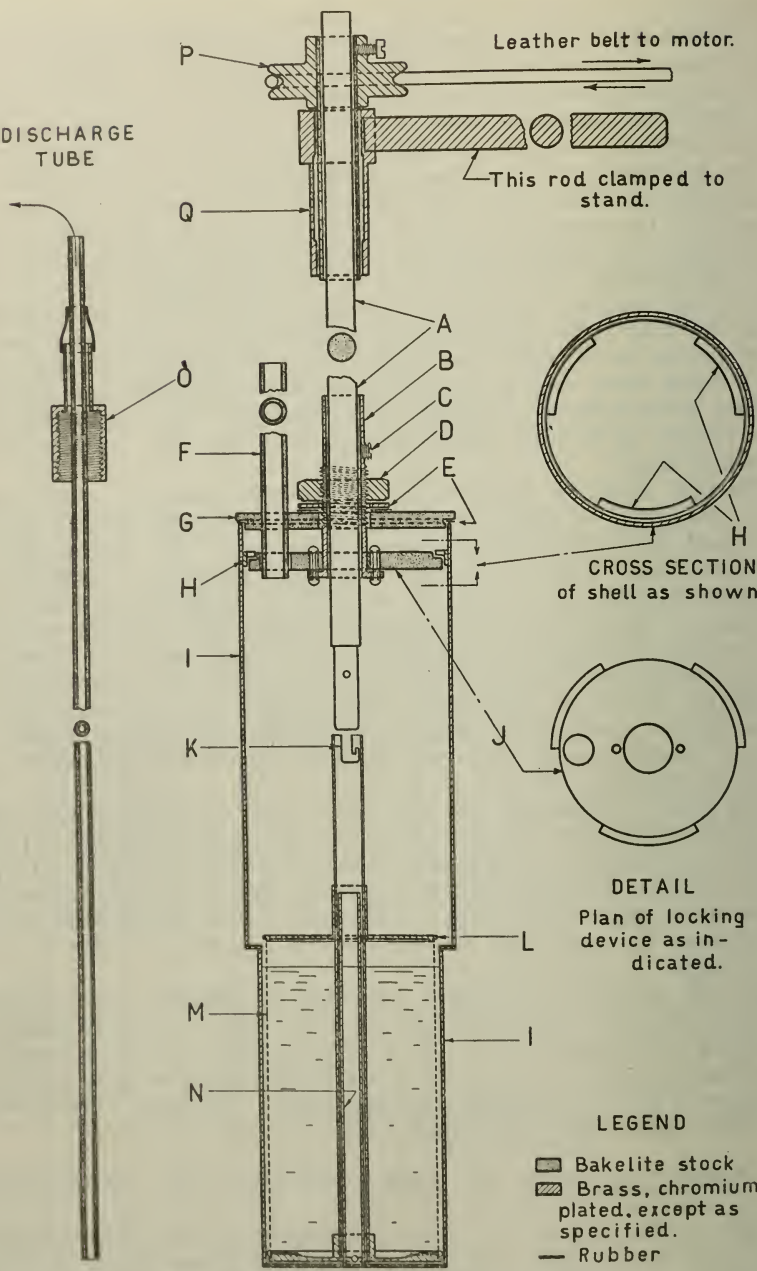

FIGURE 2.—*Centrifugal apparatus for separating solids and liquids at low temperatures.*

A, bakelite shaft; *B*, metal bearing; *C*, set screw for clamping basket in raised position; *D*, nut for drawing together two bakelite disks, *G* and *J*, to lock cover in position; *E*, rubber gaskets; *F*, bakelite vent tube tight in *G* but not attached to *J*; *G*, bakelite disk forming cover of centrifuge; *H*, brass cleats attached to shell and against which lower disk presses when cover is locked in position; *I*, shell of centrifuge; *J*, bakelite disk; *K*, bayonet lock for attaching shaft *A* to tube shaft of basket; *L*, removable metal cover of basket; *M*, centrifuge basket; *N*, bearing tube attached to bottom of shell *I* and having small holes in it flush with the bottom to admit liquid; *O*, brass cap for making discharge tube tight to *D* after removal of *A*; *P*, pulley for turning shaft; *Q*, metal bearing.

shell by a slight turn and the upper bakelite disk *G* was drawn down tightly against the top of the shell by the nut *D*.

The centrifuge basket was constructed of aluminum with perforated walls having about 700 holes per square inch. It was equipped with a removable top, *L*, to prevent splashing of the contents. It fitted snugly into the lower and smaller section of the centrifuge shell. The upper section of the shell was approximately 5 cm longer than the basket and had a diameter about 1 cm greater than that of the lower section. The tube shaft of the basket fitted over tube *N* below and into *B* at the top. Its upper end terminated in a bayonet lock, *K*, for attachment to the bakelite shaft. The small holes in *N*, which were bored flush with the bottom, allowed entrance of liquids into the shaft.

For recovery of the propane and methane so that they could be used again, the apparatus shown in figure 3 was employed. It consisted of a manifold to which small brass cylinders, of about 75 to 100 ml capacity, containing the samples could be attached, a simple trap for condensing moisture and propane, a second trap of more efficient construction for the removal of the propane from the methane as completely as possible, and finally a trap for the condensation of the methane. The first two traps were immersed in solid carbon dioxide and the third in liquid air. Several types of methane traps were used and the type shown was finally adopted because it showed the least tendency to become clogged by solid carbon dioxide, moisture, or hydrocarbon. Traps in which coiled tubes were used gave trouble from clogging though they were effective as condensers. The trap was of such capacity that enough methane could be collected in it to fill the lower section of the centrifuge.

V. OPERATION OF THE APPARATUS

The number of steps involved in the process makes it imperative to conserve time and energy if much material is to be treated. The operation will consequently be described in considerable detail.

The usual precaution in the matter of drying the apparatus before cooling should be observed to avoid clogging of tubes and sticking of moving parts. If the centrifuge is not dried between runs the basket is likely to freeze to the bottom. It can sometimes be loosened, however, when the propane and hydrocarbon mixture is added. To save liquid air, precooling was done as far as possible with solid carbon dioxide. Thus, the dewar tubes, the sample to be treated, the centrifuge cylinder, and the methane receiver were all cooled in this way before the addition of liquid air. The subsequent operations were usually performed in the order listed below:

1. Set up the condensing train as shown in figure 3, making sure that all outlets are closed, and allow the methane to condense under as much pressure as possible without causing the liquid air to spill. For condensing fresh methane the liquid air trap may, of course, be connected directly to the supply without intervening carbon dioxide traps.
2. Collect a volume of propane about equal to the volume of hydrocarbon to be treated and add it to the cold hydrocarbon.
3. Cool the centrifuge shell with liquid air and transfer to it the methane from the trap, as soon as the trap has been completely filled. Cessation of boiling of the liquid air is an indication of this, although

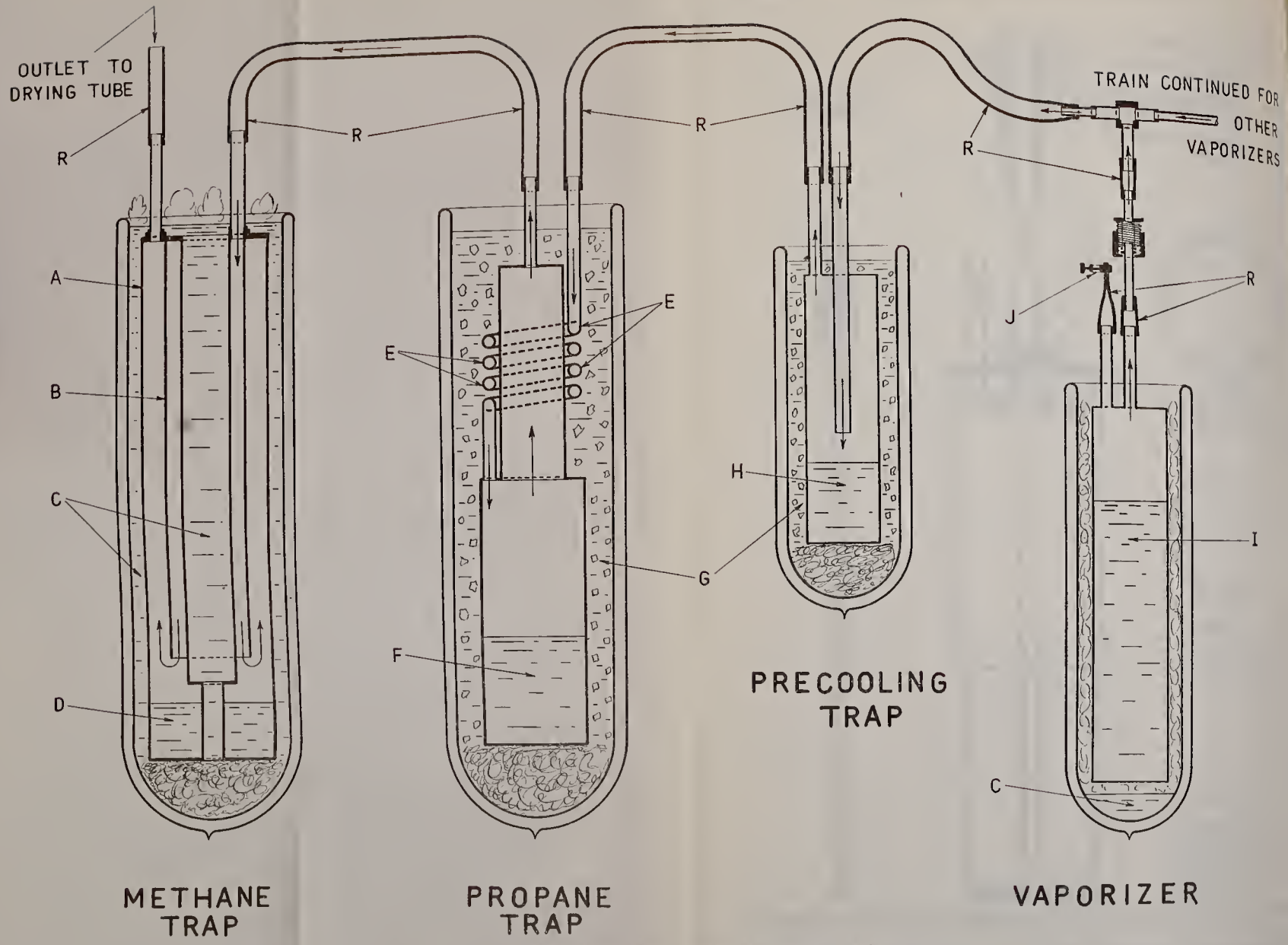

FIGURE 3.—*Condensing system for rectifying the low-boiling solvents.*

A, shell of methane trap; *B*, inlet skirt; *C*, liquid air; *D*, liquid methane; *E*, metal coils; *F*, liquid propane; *G*, solid CO_2 in cryostat liquid; *H*, propane and ice; *I*, liquid fraction from centrifuge; *J*, pinchclamp; *R*, pressure tubing.

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uncondensed gas sometimes collects in the trap and prevents further entrance of methane. If the outlet of the trap is opened slightly, the gas will escape; or if the trap is full, a small amount of liquid will be ejected.

4. Transfer the methane to the centrifuge as shown in position I of figure 4. The methane trap should be opened carefully to the atmosphere before it is disconnected from the methane supply, since uncondensed gas sometimes collects in the trap and blows liquid methane out. Before attempting to pour the methane, the exit tube should be freed of frozen material by forcing a brass rod into it. To aid in directing the stream of methane, it is convenient to attach a short bent glass tube to the exit tube. The inlet tube should be clamped shut during pouring.

5. Cool the mixture of propane and hydrocarbon to liquid air temperature and force it slowly through a siphon into the methane, which should be continuously stirred by means of a stirring rod, as shown in position I of figure 4. During this process the bakelite shaft should be in place in the central tube shaft of the centrifuge basket, since methane is sometimes squirted from the tube by a percolator action. Addition should be stopped as soon as the mixture begins to thicken. The addition of too much material results in the formation of a mass which is too thick to centrifuge properly. It has been observed that the fog which forms initially above the surface of the liquid frequently disappears when the precipitate begins to form. As mentioned before, the formation of a glassy mass can sometimes be prevented by enriching the added mixture with propane.

6. Assemble the centrifuge as shown in position II of figure 4; slide the precooled aluminum cover down the shaft to the basket, lock the bakelite cover tightly in position, and mount for spinning in some manner such as that indicated in figure 2. The cover aids in strengthening the basket but is not necessary. The basket should be raised to its spinning position slowly to prevent splashing or boiling of methane. The exit of the methane trap of the condensing system should be opened to the atmosphere through a drying tube, and it is well to test the system for free passage by blowing into one of the inlets to the manifold before attaching it to the centrifuge. Stoppages occur in the small inlet tubes of the traps and can be opened by forcing a warm wire or rod into them.

7. The centrifuge must be rotated in such direction that the "bayonet lock" will remain fixed. Centrifuging should be begun slowly to avoid boiling the methane. It need not be very rapid (about 300 to 400 r.p.m.) and should be continued for a minute or two. It should be stopped slowly or the momentum may cause the basket to unlock from the shaft.

8. Demount the centrifuge and remove the liquid fraction, as shown in position III of figure 4. This is done by pulling up the basket as shown, so that the tube shaft projects into *B* (of fig. 2), where it is held by the screw *C* (of fig. 2) or by friction. The bakelite shaft can then be removed, leaving an opening to the bottom of the apparatus into which the siphon tube can be inserted. The sample cylinders *V* must be cooled nearly to liquid air temperature and should be connected temporarily to the manifold of the condensing system by a rubber tube connection while the hydrocarbon is being forced into them.

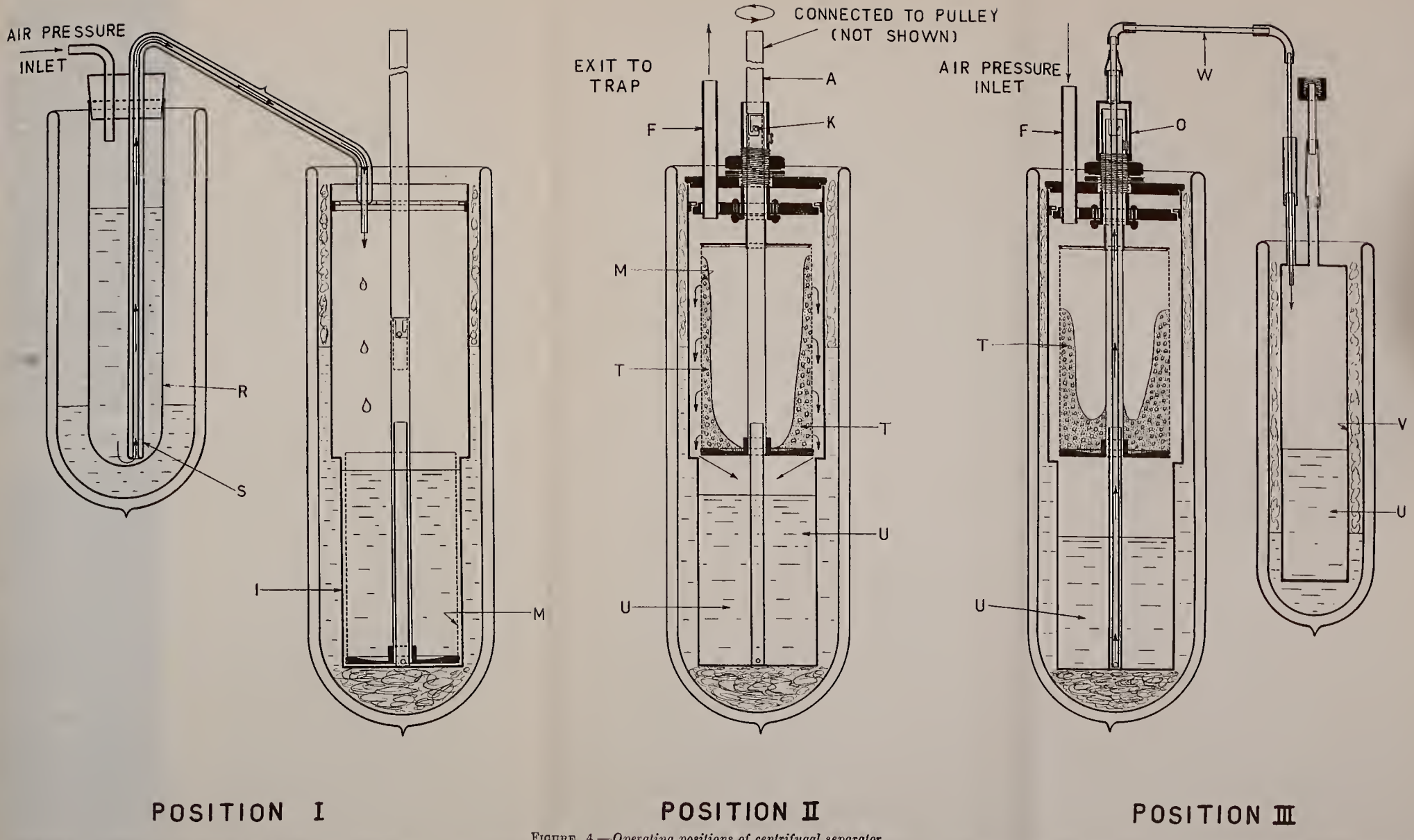

FIGURE 4.—*Operating positions of centrifugal separator.*

4, bakelite shaft; *F*, vent tube; *I*, centrifuge shell; *K*, bayonet lock; *M*, centrifuge basket; *O*, cap of siphon apparatus; *R*, glass test tube containing hydrocarbon-propane mixture; *S*, vacuum jacketed glass tube; *T*, solid phase; *U*, liquid phase; *V*, brass tube for receiving liquid phase (shown as "vaporizer" in fig. 3); *W*, glass tube forming part of emptying siphon.

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9. Attach the cylinders to the manifold of the condensing apparatus, as shown in figure 3. Remove the siphon from the centrifuge, close the opening with a stopper or a screw cap, and attach it to the manifold through *F*.

10. Remove the cylinders gradually from the liquid air until most of the methane has boiled out. Then remove the centrifuge cylinder from its tube. This is done because the liquid fraction contained in the small cylinders are richest in methane, which should be condensed first before the propane-rich gas which is liable to clog the liquid air trap is evolved.

It was found that about 50 cubic feet of natural gas was required for one experiment with the larger apparatus. About three quarters of this could be recovered by careful manipulation. The entire process as described required about 3½ hours for completion. By starting with the methane trap partially filled, however, the time was considerably shortened, and it was found possible to run three successive experiments in a period of about 8 hours.

When the work was stopped overnight the methane trap was attached to an empty tank of sufficient capacity to hold all the methane if necessary, the outlet of the trap to the atmosphere closed, and the trap covered with liquid air. Any methane which evaporated was received by the tank, thus avoiding loss as well as danger of escape into the atmosphere of the room. For storage over more prolonged periods the contents of the trap were allowed to boil into a storage reservoir. All the traps and tanks were tested at 60 pounds pressure occasionally to detect the development of leaks or weaknesses.

VI. ISOLATION OF 2-METHYLHEPTANE FROM PETROLEUM

The fractions of petroleum which, after careful distillation, boiled between 115° and 120° C. were investigated on a small scale, as described above, and solid phases were found to separate from several of the fractions. The material distilling near 116° was found to yield a precipitate with an index lower than the mother liquid. Further treatment yielded a sample of material which had a lower index of refraction than any of the probable constituents of petroleum likely to be found in this boiling range except 2-methylheptane.

The material [3] on which this work was done had been distilled once in a 20-plate metal laboratory still, followed by 10 distillations in 10-plate glass stills, 1 distillation in a 30-plate glass still under atmospheric pressure, and 1 under 726 mm of Hg. These distillations were made in the course of the isolation of the *n*-octane from petroleum as completely as possible by repeated distillation and crystallization.[4] Line No. 3 of figure 5 shows the distribution of material over the boiling range before the removal of *n*-octane. It is to be observed that most of the material from which the 2-methylheptane was later isolated was included along with *n*-octane and other constituents in the cut boiling between 118° and 128° C. After the *n*-octane represented by the dotted area was removed by crystallization, the residues were redistilled 10 times, and the distribution on the thirteenth distillation is shown by line 13. Most of the peak (line no. 3) between

[3] For description and properties of the petroleum, see Washburn, E. W., Bruun, J. H., and Hicks, M. M., B.S. Jour. Research, vol. 2, p. 469, table 1, 1929.

[4] All distillations were directed by S. T. Schicktanz, research associate representing the American Petroleum Institute.

118° and 128° was replaced by a somewhat narrower peak between 115° and 120°. The lower boiling material of this peak possessed a low refractive index approaching that of 2-methylheptane.

Beginning with the most promising fractions (those boiling at about 116° during the distillation or at about 117° in a Cottrell apparatus at atmospheric pressure) it was found possible to obtain filterable crystals from all of the material of the last distillation boiling between 115° and 117°. In all about 6.5 liters of material was treated by the process described, and 1,550 ml of material rich in 2-methylheptane was obtained. The average refractive index of the original material was 1.401^{20}, while that of the product was 1.3980^{20} and that of the residue 1.403^{20}. Redistillation of this residue yielded about 1,100 ml of material, which was treated a second time and yielded an additional 280 ml of product. This

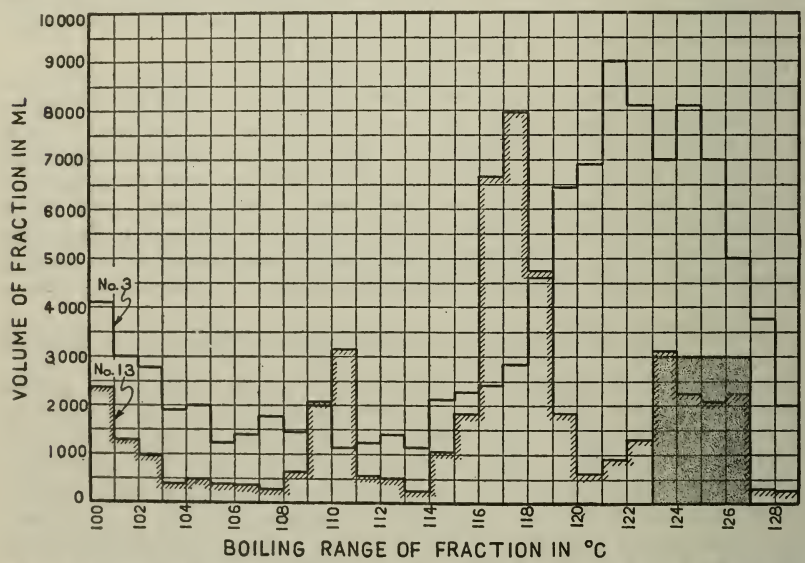

FIGURE 5.—*Graph of the distillation of the fractions of petroleum boiling between 100° and 129° C.*

product was sufficiently pure to show very definite arrests in the cooling curves, from which it was possible to estimate the quantity of pure material present. Because of the difficulty and expense involved, no attempt was made to purify the entire quantity of product.

VII. PROPERTIES OF 2-METHYLHEPTANE

In order to establish the identity and properties of the hydrocarbon isolated, 200 ml of "product" was given further successive treatments until the freezing point and refractive index ceased to change. This required six additional treatments, and 60 ml of purified material was obtained. Table 1 gives the observed properties of this sample (lot I), together with those of the other lots of product and the data for a synthetic sample reported in the literature. Figure 6 shows the melting and freezing curves of lot I. No data concerning

the freezing point were obtainable from the literature, and it will be observed that the refractive index of lot I is lower than that reported by Clarke, while its boiling point is higher. These discrepancies may probably be attributed to differences in the methods of measuring the properties, since the properties of the *n*-octane previously isolated from petroleum differ from those reported by the same author in the same directions and to approximately the same degree. The boiling points reported in the table were determined by means of a Cottrell boiling-point apparatus. The refractive indices were determined on a calibrated abbé split prism refractometer. The density was determined by pycnometers similar to the Ostwald-Sprengel type of about 20 ml capacity. A resistance thermometer previously described by Mair [5] was used for all freezing-point determinations.

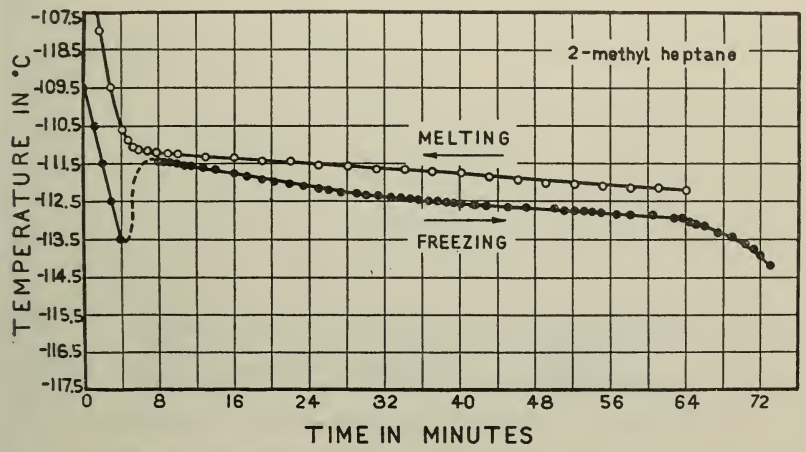

FIGURE 6.—*Melting and freezing curves of 2-methylheptane.*

This thermometer was calibrated in accordance with the specifications for the International Temperature Scale adopted in 1928.[6]

TABLE 1.—*Physical properties of 2-methylheptane*

Material	Normal boiling point	Freezing point (in dry air)	Refractive index n_D^{20}	Specific gravity	Purity	Volume
	°C.	°C.			*Mole percent*	*ml*
Synthetic [1]	116	----------	1.3967	0.7035_{15}^{15}	----------	--------
Lot I	117.2	−111.3	1.3949	$.6985_{20}^{20}$	97	60
Lot II	117.7	−117.0	1.3986	----------	78	430
Lot III	117.5	−118.3	1.3985	----------	73	420
Lot IV	117.5	−120.1	1.3995	----------	67	470
Lot V	117.7	−116.6	1.3978	----------	79	400

[1] Date reported by Latham Clarke, J.Am.Chem.Soc., vol. 31, p. 107, 1909.

[5] Mair, B. J., B.S. Jour. Research, vol. 9, p. 457, 1932.
[6] G. K. Burgess, B.S. Jour. Research, vol. 1, p. 635, 1928.

Since no data on the heat of fusion were obtainable, the molal lowering of the freezing point was determined by the addition of a known weight of toluene to the purest sample. This corresponded to a heat of fusion of approximately 2,200 g-cal/mol and from this the approximate purity of the other samples was calculated. The purity of the best sample (lot I) was estimated by assuming that the concentration of impurity in the solution had doubled at the midpoint of the freezing curve.

The infrared absorption spectrum as observed by U. Liddel, of the Fixed Nitrogen Laboratory, U.S. Department of Agriculture, is shown in figure 7.

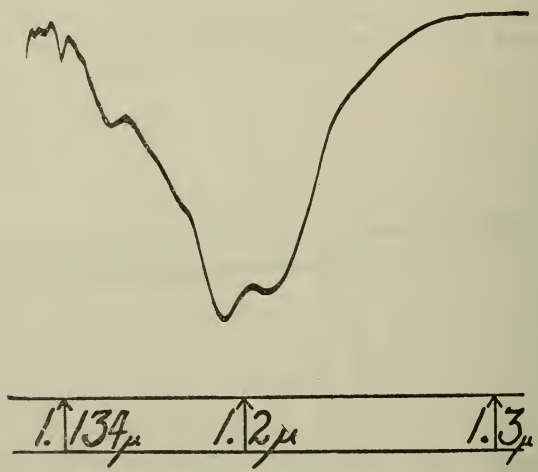

FIGURE 7.—*Infrared absorption curve of 2-methylheptane.*

The absorption band of iso-octane, composed of the second overtone frequencies of the fundamental carbon-hydrogen oscillation band around 3.4 μ. This is a portion of an automatically recorded energy-transmission curve through a 1 cm cell of iso-octane; the fine sharp absorption around 1.134 μ being due to atmospheric water vapor.

VIII. ESTIMATION OF THE 2-METHYLHEPTANE CONTENT OF CRUDE PETROLEUM

From the quantity of material isolated and an estimation of the losses incurred, it is concluded that the concentration of 2-methylheptane in the original curde oil was not less than 0.15 per cent.

IX. ACKNOWLEDGMENTS

The author acknowledges the technical advice of E. W. Washburn, Director of the American Petroleum Institute Project No. 6, and the assistance of J. D. White and F. W. Rose. He is also indebted to the Washington Gas Light Co. for supplying the natural gas from which the methane was obtained.

WASHINGTON, February 20, 1933.